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## The role of concurrent chemical and physical processes in determining the maximum use temperature of thermosetting polymers for aerospace applications

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### Introduction

Thermosetting polymers such as epoxies, polyimides, bis-maleimides, phthalonitriles, and cyanate esters have become widespread in aerospace applications due to their lower densities and ease of processing compared to metals. Although epoxy resins dominate, their maximum use temperatures are too low for some applications, particularly those involving propulsion, control surfaces, and electronic systems.<sup>1</sup> Thus, the defining characteristic that drives the use of most other types of thermosetting polymers in aerospace applications is the maximum use temperature. Traditionally, the maximum use temperature for a thermosetting polymer is determined by performing a dynamic mechanical thermal analysis (DMTA), using a pre-conditioned sample heated at no more than 5 °C/min. The maximum use temperature is based on the glass transition temperature (which in these experiments is actually the mechanical softening or weakening point no matter what the mechanism) observed under a variety of sample pre-conditions, minus a factor of safety designed to account for material and process variability as well as any unidentified causes of performance degradation.

For many thermosetting polymers (particularly those that exhibit excellent thermo-chemical stability and require thermal cure at temperatures greater than the maximum use temperature) the method works well. There is, however, a continuing drive to utilize materials with the combination of a high use temperature and a low cure temperature. In addition, for applications in which exposure to high temperatures is short-term rather than long-term, there is a desire to utilize less expensive and easier-to-process materials with reduced thermo-chemical stability. For these materials, the determination of the maximum use temperature must take into account chemical effects that are often not considered in a purely mechanical analysis. These result from concurrent residual cure and thermo-chemical degradation in addition to mechanical softening. Herein we report on our efforts to better determine the maximum use temperatures of thermosetting polymers through a combination of alternative thermo-mechanical analyses. We show that thermal cycling and attention to heating rates can often provide more reliable results with a minimum of additional effort.

### Experimental

**Materials.** Cyanate ester resins, and particularly the dicyanate ester of Bisphenol E, are notable for an unmatched combination of low cure temperature and high use temperature,<sup>2</sup> while possessing lower thermo-chemical stabilities than, for instance, thermosetting polyimides.<sup>3</sup> They are therefore outstanding candidates for the study of concurrent cure, softening, and chemical degradation and its effect on maximum use temperatures. Primaset® LECy, a commercial form of the dicyanate ester of Bisphenol E, was therefore purchased from Lonza, AG and used as received. Copper(II) acetoacetone from ROC/RIC and nonyl phenol (Technical Grade) from Aldrich were combined to produce a liquid catalyst.

**Sample Preparation.** Catalyst batches were prepared by blending 30 weight parts nonyl phenol with one weight part copper (II) acetoacetone at 60 °C until dissolved. Batches were discarded after 3 days. Cyanate esters were melt blended (using 2 phr catalyst) and degassed at 95 °C for 30 minutes at 300 mm Hg. The samples were then poured into a 3.5" x 3" metal-framed vertical dual glass plate mold with a 1.5 mm gap. The cure cycle was 1 hour at 120 °C followed by 24 hours at 175 °C, with an optional post-cure for 2 hours at 240 °C. All curing and post-curing was done under nitrogen. Ramp rates between the long dwells were ~5 °C/min. Note that the as-blended level of Cu(II) was 160 ppm by weight.

**Characterization.** Oscillatory thermo-mechanical analysis was performed on a TA Instruments Q400 series using the standard dry cylindrical probe on pieces of the cured samples measuring approximately 10 mm x 10 mm x 1.5 mm thick. A preload force of 0.2 N was used to hold the samples in place. Force modulation of aplitude 0.1 N at a frequency of 0.05 Hz (maintaining an average force of 0.1 N) was used to investigate the samples. To determine thermal lag, the temperature was cycled at the desired ramp rate between limits of 50 °C and 150 °C twice. Generally, the observed thermal

lag ranged from 1 - 5 °C, and all data shown have been corrected for this estimated thermal lag. After the thermal lag determination, each sample was heated to 350 °C then cooled to below 200 °C in multiple ramp cycles. The ramp rates used varied from 2 °C/min. to 10 °C/min. Further information on the TMA testing and analysis methods are provided elsewhere.<sup>4</sup> In addition to TMA testing, the results discussed below make indirect use of differential scanning calorimetry (DSC), density measurements, thermogravimetric analysis, FT-IR analysis, and moisture uptake measurements that have been performed previously on the material, with the results reported elsewhere.<sup>5</sup>

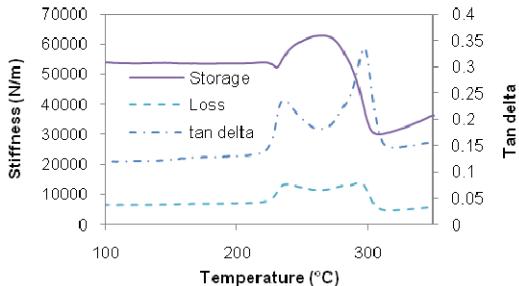
### Results and Discussion

Normally, it is expected that, once corrected for thermal lag, the thermo-mechanical behavior and glass transition temperature ( $T_g$ ) of a thermosetting polymer will be nearly independent of the heating (or cooling) rate. However, as shown in Figures 1, 2, and 3, markedly different oscillatory TMA traces were generated for Primaset® LECy cured to 185 °C simply by using heating rates of 2, 5, and 10 °C/min. (during the first heating ramp to 350 °C), respectively. The "as-cured"  $T_g$  of the sample (240 °C) was seen clearly only at 10 °C/min. At 5 °C/min., an artificially broad  $T_g$  with a peak well above the "as-cured" value was obtained. At 2 °C/min., the "as-cured"  $T_g$  generates only a small secondary peak. The strong dependence on  $T_g$  (as determined by the peak in the loss component of the stiffness) on heating rate is illustrated clearly in Figure 4. The  $T_g$  seen at low heating rates corresponds well to values determined by DSC after heating to 350 °C to obtain full cure. Thus, these samples clearly underwent residual cure *in-situ*, greatly complicating the task of measuring the "as-cured"  $T_g$ . At 5 °C/min., the rate at which the sample  $T_g$  rose due to *in-situ* cure was similar to the heating rate, creating the artificially broad transition.

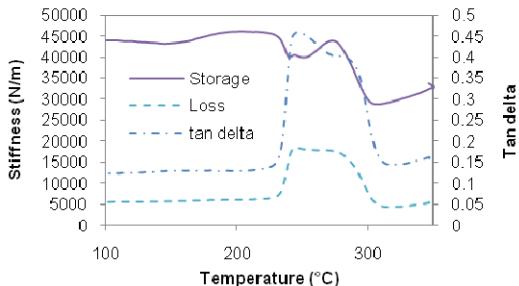
These results demonstrate that for cyanate ester resins, and in fact for any thermosetting material in which the glass transition temperature can significantly exceed the cure temperature, care must be taken in the selection of heating rates to avoid incorrectly measuring  $T_g$  values. Based on the diBenedetto equation (which has been validated for Bisphenol E-based cyanate esters),<sup>6</sup> it can be shown that the *in-situ* cure rate for the LECy was around 0.5% per minute at around 240 °C. Since this type of *in-situ* cure typically takes place at high conversion under non-isothermal conditions, it would be difficult to estimate the rate *a priori*. Thus the best approach would seem to involve checking DMTA or TMA results in these cases by using multiple heating rates.

Further insight into concurrent *in-situ* cure, softening, and degradation processes can be obtained by incorporating multiple heating and cooling cycles into a thermo-mechanical experiment, as illustrated by Figure 5. The figure shows the  $T_g$  values as a function of the number of times the sample has been cycled past 300 °C (not counting sequential heating and cooling separately). After only once, all of these samples were near complete cure. Interestingly, samples that were post-cured did not achieve a higher final  $T_g$ . These results are in accordance with the data of Goertzen and Kessler,<sup>7</sup> and could indicate either physical isolation of uncured cyanate ester groups due to overly rapid cure, or the effect of increased side reactions and thermal degradation during post-cure. In addition, the data do show a slightly declining trend for the  $T_g$  as the number of cycles increases, most likely indicating that a very small amount of thermal degradation did take place. It should be noted, however, that the ramp rates utilized provided roughly 1-5 hours of exposure to temperatures in excess of the post-cure temperature, and produced only roughly 10% of the decrease in  $T_g$  seen in the samples that were post-cured for two hours. Thus, if thermo-chemical degradation were the primary cause of the lower  $T_g$  values in the post-cured samples, it would need to be highly dependent on conversion and/or the relative value of  $T_g$  during post-cure, rather than just a simple matter of exposure to elevated temperatures.

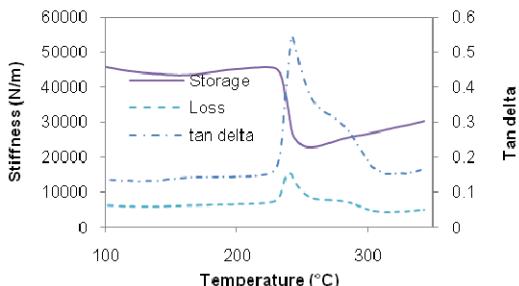
Although the previous examples illustrate how the use of multiple heating rates and multiple thermal cycles can greatly aid in the interpretation of thermo-mechanical data for systems undergoing simultaneous *in-situ* cure, chemical degradation, and softening, other methods can also be very helpful. Comparative FT-IR, for instance, though not quantitatively accurate as a means of determining extent of cure for many systems in the solid state without special calibration procedures, can provide a quick indication of whether or not a sample has undergone substantial *in-situ* cure. Similarly, DSC studies carried out at the heating rates of interest may also detect the heat released by *in-situ* cure and thermal degradation. At high conversions, though, thermo-mechanical methods can be used in combination with the diBenedetto equation<sup>8</sup> to estimate the degree of cure to within 0 - 5%, which is about an order of magnitude better than FT-IR or DSC. Thus, a careful and more extensive investigation using thermo-mechanical analysis is likely to provide the most useful data in the situations commonly encountered in aerospace applications where the maximum use temperature of a high-performance thermosetting resin at nearly full conversion is a key performance parameter.



**Figure 1.** Oscillatory TMA of catalyzed Primaset® LECy using a ramp rate of 2 °C / min.



**Figure 2.** Oscillatory TMA of catalyzed Primaset® LECy using a ramp rate of 5 °C / min.

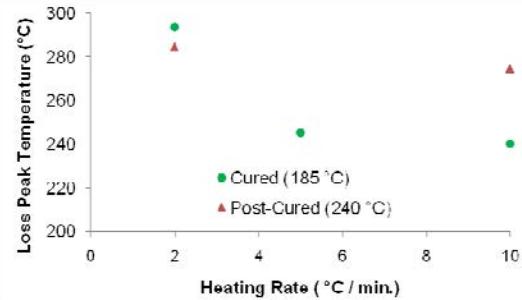


**Figure 3.** Oscillatory TMA of catalyzed Primaset® LECy using a ramp rate of 10 °C / min.

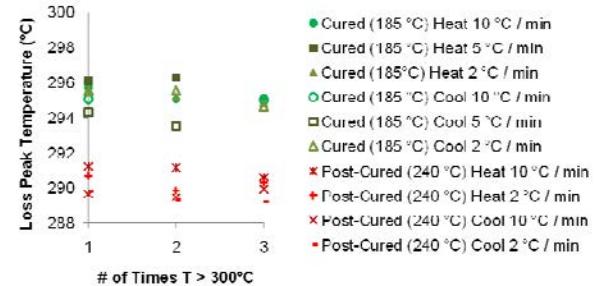
## Conclusions

For thermosetting polymers with glass transition temperatures that exceed their final cure temperatures, and for which short-term thermal stability considerations dominate, such as cyanate ester resins, a traditional thermo-mechanical analysis can easily produce an inaccurate estimate of the maximum use temperature. In these situations, chemical rather than mechanical effects, such as *in-situ* cure and thermo-chemical degradation, can take place concurrently with mechanical softening and significantly affect thermo-mechanical measurements. In order to obtain accurate data on parameters such as  $T_g$  that are crucial for the determination of maximum use temperatures, a much higher heating rate than normal may be needed, and it is highly advisable to use multiple heating rates to check for *in-situ* cure. In addition, the use of multiple heating and cooling cycles can elucidate the effects of thermo-chemical degradation. For Primaset® LECy, a heating rate of 10 °C / min was found to be sufficient to avoid significant *in-situ* cure for  $T_g$  values around 240 °C. Although the effects of thermo-chemical degradation were detectable, the resultant changes in  $T_g$  were less than 1 °C for the experimental parameters investigated.

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**Figure 4.** Glass transition temperature on first heating of catalyzed Primaset® LECy as a function of ramp rate.



**Figure 5.** Glass transition temperature through multiple heating and cooling cycles of Primaset® LECy at multiple ramp rates.

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